Traitements pyrométallurgiques des nodules polymétalliques.

Pyrometallurgical processing of polymetallic nodules

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INTRODUCTION

"The vastness of the oceans has always fired the imagination : continents swallowed up with their fabulous treasures, Eldorados at the edge of ever-changing horizons, galleons laden with gold whose wrecks are strewn over the sea bed.

The true riches of the ocean are probably quite different and perhaps even more surprising."

J.P. Lenoble and P. Rogel
Annales des Mines
March 1974.

The polymetallic nodules discovered on the ocean floors as far back as 1873 came to be considered as a possible source of supply of metals only after almost a century had passed.

Although exploration of the ocean deeps is far from complete, extrapolation of results already obtained has led to the conclusion that they represent an immense reserve of ores for metals as essential to present-day industry as manganese, nickel, colbalt and copper.

Depending on the evaluations made and the criteria employed to assess the economics of winning and working (concentration, density per square metre, depth, etc.), the estimates of reserves amount to hundreds or thousands of years of use at the present rate.

LOCATION, COMPOSITION AND EXTRACTION

The pattern of geographical distribution of nodules is extremely wide-ranging and varied (cf. Fig. 1).

Currently, the most interesting area is the North Pacific between the Hawaiian islands and the West Coast of the USA. Here, the density of nodules on the sea floor and contents of useful substances are particularly high. It must however be said that this is also the most highly explored area of any of the ocean beds, so that there is probably a connection.

The nodules are invariably located in very deep water (4000 to 5000 metres), far enough from land to be unaffected by the abundant continental detrital deposits.

Their density on the sea bed is in the region of 5 kilograms per square metre (expressed as dry weight) for the richest fields.

Nodules have been formed by undersea hydrothermal deposition around a seeding nucleus.

It is assumed that this has involved the precipitation of manganese hydroxide which has enmeshed various ions such as iron, nickel, cobalt and copper.

The nodules are contaminated to varying degrees by argillaceous or argillocalcareous sedimentary deposits.

Nodule composition varies quite a bit from field to field. The nodules of the Pacific are, on the whole, richest in elements of interest (cf. Fig. 2). Those of the North Pacific, the source of the samples on which we have been working, are particularly rich in manganese and nickel and in copper.

The origin of the nodules explains why they come to be so highly enriched in certain elements (manganese, nickel, cobalt, copper, lead and iron) as compared to typical natural rates of occurence in continental rocks (cf. Fig. 3). It also explains the very porous layered structure (onion-skin structure) and the high contents of absorbed water and alkali halides.

Nodules therefore have to be mined at locations meeting at least three criteria, i.e. :
- High density of nodules on the sea bed
- High concentrations of wanted elements
- Minimal sedimentary deposition

Recovery is probably the problem involving the greatest number of technological difficulties, almost on a par with those to be resolved in the exploration of space.

A great variety of systems have been conceived, from self-contained vehicles communicating with a floating platform, to the continuous line bucket (CLB) system connected to one or two vessels, and including hydraulic systems.

Very few have been tried out and, to date, no start has been made on any sort of commercial-scale operation.

IMPORTANCE OF NODULES

From these observations, plus the fact that onshore' reserves are far from being exhausted, it can be concluded that research on the mining, metallurgy and chemistry of nodules will not yield any industrial results before the twenty-first century.

Nonetheless, what is sure is that nodules will, in time, constitute an essential source of rare metals and of considerable wealth.

A point to note is that manganese, although much less valuable as such than the three other metals, is present in such concentration that it accounts for two-thirds of the total value of the metals in these deposits. Nickel accounts for more than one-fifth of the remainder (cf. Fig. 4).

In terms of quantities available, there are also considerable differences according to the metal considered, especially when availabilities are compared with world demand.

For instance, supposing world demand for manganese were to be met to the extent of 100 % by mining nodules, then 25 % of demand for nickel would also be covered, but only 2 % of demand for copper, while almost twice as much cobalt be produced as is currently used by industry worldwide (cf. Fig. 5).

This potential source of wealth, plus the certainty that it will one day have to be exploited, has prompted major industrial or state-owned concerns working on a long-term basis to get together to set up joint research organisations assigned the task of devising and quantifying processes for the treatment of nodules.

Such international ventures include the OMA consortium, the KCC consortium, the OMI consortium, the OMCO consortium, AFERNOD, the CLB syndicate, the DOMA association, etc., from which government interests are not absent.

Each association has undertaken research in the three significant areas of :
- nodule location
- nodule extraction
- nodule processing

NODULE TREATMENT PROCESSES

This is an area in which a distinction has to be drawn between two major categories of process, i.e. :

i) The "three metals" processes, which are concerned solely with the recovery of nickel, cobalt and copper.

ii) The "four metals" processes, the economics of which are based on the simultaneous production of manganese and of the three "noble" metals in marketable form.

The methods employed in these various processes encompass the full range of techniques for the extraction and processing of metals, e.i. :
- hydrometallurgy
- electrolysis
- solid phase pyrometallurgy
- molten phase pyrometallurgy

More often than not, several of these techniques are employed in conjunction in one and the same process.

The "three metals" processes invariably involve hydrometallurgy and electrolysis. Since they neglect almost two-thirds of the total market value, there is every chance that their economics will be less firmly based than for the processes which also recover manganese.

The "four metals" processes are of two kinds, either :

a) hydrometallurgical and electrolytic - these produce manganese as the pure metal, for which the price is high and the market narrow ;

or :

b) pyrometallurgical - the end-result of which is separation of the manganese as an alloy which is invariably to some extent contaminated by copper.

OBJECTIVES OF PECHINEY ELECTROMETALLURGIE (PEM)

In an area in which its expertise is fully recognised, PEM (formerly styled SOFREM, Société Française d'Electrométallurgie), has investigated and developed a novel process for the treatment of polymetallic nodules making maximum use of molten-phase pyrometallurgy, whereby it has set itself the objectives of :

First, extracting the four commercially valuable metals from the nodules, at maximum possible efficiency, in the form of a pair of intermediate products featuring the highest possible concentrations of the target elements, i.e. :

i) an alloy of varying iron content, containing the three noble metals - nickel, cobalt and copper - and the least possible quantity of manganese.

ii) a slag containing the bulk of the manganese and very little nickel, cobalt and copper.

In the second instance, the alloy would undergo a process of chemical or electrochemical refining, while the manganese slag would be processed in the electric furnace to obtain, for example, a silicomanganese or a high-carbon ferromanganese.

TESTS CARRIED OUT AND METHOD ADOPTED

Our tests comprised the following steps :

- Investigation of preliminary treatment (conditioning) of nodules.
- Investigation of controlled reduction of nodules to obtain the alloy (i).
- Investigation of purification of the slag (ii) by reduction treatment to remove nickel, cobalt and, most importantly, copper.
- Investigation of alloy concentration and removal of manganese by oxidative treatment.

The nodules are wet, hydrated and contain alkali metals. A number of variant conditioning processes were tried out, each comprising certain of the following distinct operations :

- Size reduction by grinding to 100 microns (after rough drying).
- Acid washing of the powder followed by a water rinse to remove salts of the alkali metals.
- Drying at 110°C to drive off excess moisture.
- Agglomeration of the powder on a pelletising machine.
- Calcination at 650°C to remove combined water (from hydrates).
- Incorporation of carbon (coke fines or fuel oil) at the pelletising stage.
- Prereduction of carbonaceous pellets at the calcinanation stage.

These preparatory treatments yield one of three kinds of product :

A - dehydrated whole nodules
B - pellets free of alkali metals and simply dehydrated
C - pellets partially reduced to the metallic condition (cf. Fig. 6)

All three are amenable to reduction in the molten state designed to effect the separation of nickel, cobalt and copper in a metallic phase and manganese in an oxidised phase.

The complex procedure required to remove the alkali metals avoids the vaporisation and release of sodium and potassium at the reduction stage, which would otherwise require the reduction furnace to be equipped with much more sophisticated pollution control facilities.

Following our initial reduction attempts, it transpired that the dehydrated nodules exhibited much higher reactivity than the pellets obtained after purification treatment, whether or not prereduced, and that this was true for very similar analytical data.

Our subsequent investigations were carried out solely on whole nodules.

Table I (appended) sets out analytical data for the various subproducts obtained from the sample of nodules in our possession.

Our reduction tests were carried out in a 100 kVa three-phase arc furnace, brick-lined, using magnesite refractory for the walls and aluminous refractory for the hearth (cf. Figs 7 and 8).

Two methods of reduction were tried : with carbon (at this stage we employed charcoal), and with silicon (in the form of 75 % ferrosilicon). It rapidly became apparent that silicon on its own gave no better results than carbon as a reducing agent. The use of FeSi 75 at this stage was abandoned because it was more expensive and meant increased contamination by iron.

Examination of the Ellingham curves for the reactions of formation of the oxides of copper, nickel, cobalt and manganese suggests that there should be no difficulty in separating the two groups of metals (cf. Fig. 9). This is not however the case.

It will be seen that, when increasing quantities of carbon-based reducing agents are employed, copper, which should theoretically be the easiest to reduce, remains in part in the oxidised state whereas manganese starts to be reduced to the metallic state (cf. Fig. 10).

This unexpected difficulty, arising no doubt from combination of copper with an element other than in oxygen contained in the slag, compelled us to employ a more complex treatment flowsheet. The reduction had to be carried out in two stages (cf. Fig. 11), comprising :

1 - Liquid-phase reduction with carbon, yielding an alloy virtually free of manganese.
2 - More intensive reduction of the resultant slag, using silicon (as FeSi 75), yielding a slag quite free of copper (and therefore, needless to say, of nickel and cobalt).

The metal resulting from this more intensive reduction (Stage 2) contains the copper (and nickel and cobalt) remaining in the Stage 1 reduction slag. Additionally, however, it contains manganese, iron and, sometimes, silicon. It is a good reducing agent as regards NiO, CoO and CuO. It was therefore returned to the carbon-reduction furnace in place of part of the carbon-based reducing agent.

This indirect, two-stage, countercurrent reduction process enables both our objectives to be achieved simultaneously, i.e. :

- a manganese-free metal containing the noble metals (efficiencies : Ni 98,8 %, Co 97.7 %, Cu 98.6 %).
- a slag free of nickel, cobalt and copper and containing the manganese (efficiency : Mn 92.0 %).

This slag, cast as ingot, may be employed as a source of manganese in a reduction furnace in the production either of high-carbon ferromanganese or of silico-manganese.

The alloy obtained can be chemically or electrochemically processed to separate the three noble metals contained. In the example discussed, its composition could be rather lean as regards such treatment (30 % noble metals and 70 % iron). Enrichment is possible by means of oxidation (cf. Fig. 12). For instance, oxygen can be blown in by means either of a cooled surface lance or of double-wallet bottom nozzles (protected by a cooling fluid).

Depending on the desired content of noble metals, blowing treatments of varying intensity will be employed, with inter-stage dross removal. The initial slags formed, very lean in noble metals, will go to the slag-heap. Indeed, in order to achieve very high concentrations, some loss of nickel, cobalt and copper in the slag will have to be accepted ; this slag could then be recycled along with the fresh charge of nodules.

This oxidation treatment, as well as appreciably increasing the concentrations of valuable elements in the alloy, purifies it of the last traces of manganese and removes carbon.

CONCLUSIONS

Pechiney Electrométallurgie has investigated and developed a novel process for the treatment of deep-sea nodules. This work has led inter alia to the grant of a patent (French Patent Application 77.10862) entitled :

"Process for the treatment of complex metal ores containing in particular manganese and copper, such as oceanic nodules".

A novel feature of this process is the perfect separation obtained between manganese, contained in an oxidised slag, and the group consisting of nickel, cobalt and copper, contained in a ferrous alloy. The separation is effected at excellent levels of efficiency as regards each of the four commercially valuable metals.

Based on this process, we have imagined the possibilities of a plant continuously processing 200 to 230 tonnes per hour of raw nodules, which we estimate as the economic size for a project of this kind.

This plant would produce, annually, 865 000 tonnes of a slag containing 325 000 tonnes of manganese and 45 000 tonnes of an alloy containing 16 000 tonnes of nickel, 2 600 tonnes of cobalt and 8 600 tonnes of copper (cf. Fig. 13).

Although the exploitation of these immense undersea riches is not as yet one of the metals industry's immediate concerns, we felt it preferable to be ready, in this sphere as in others, to face the challenges of the close of the 20th century and the dawn of the 21st.

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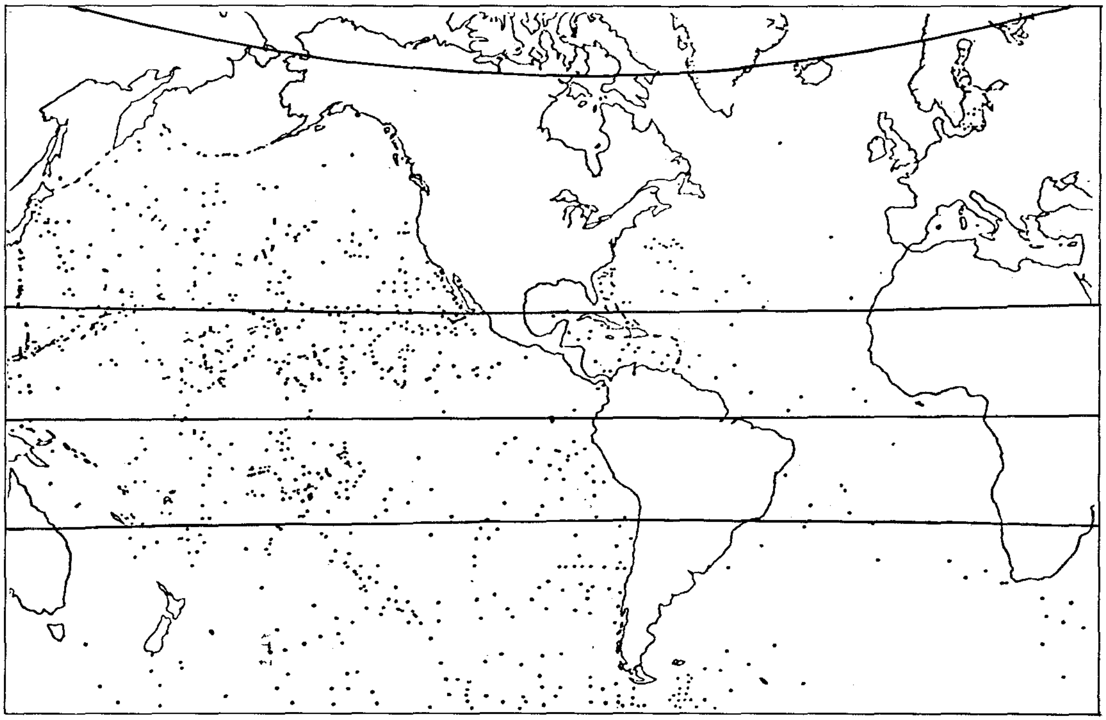
Chemical species	Composition, % w/w			
	Raw nodules	Dehydrated nodules	Pellets of washed material	Partly metallic pellets
MnO_2	24.14	35.98	36.80	7.82
MnO	8.56	12.77	13.05	40.92
Fe_2O_3	11.04	16.46	17.50	2.22
FeO	-	-	-	14.64
NiO	1.37	2.04	2.17	-
Ni	-	-	-	1.71
CoO	0.22	0.33	0.35	-
Co	-	-	-	0.28
CuO	0.73	1.09	1.16	-
Cu	-	-	-	0.93
SiO_2	10.25	15.29	16.25	17.18
MgO	2.66	3.96	4.18	4.43
CaO	2.17	3.23	3.37	3.57
Na_2O	2.15	3.20	0.08	0.06
K_2O	0.47	0.70	0.39	0.37
Cl	0.49	0.73	0.07	0.07
Various oxides	2.83	4.22	4.63	5.36
Moisture	32.92	0	0	0
Additional oxygen (calc. on Ni, Co and Cu)	-	-	-	0.32

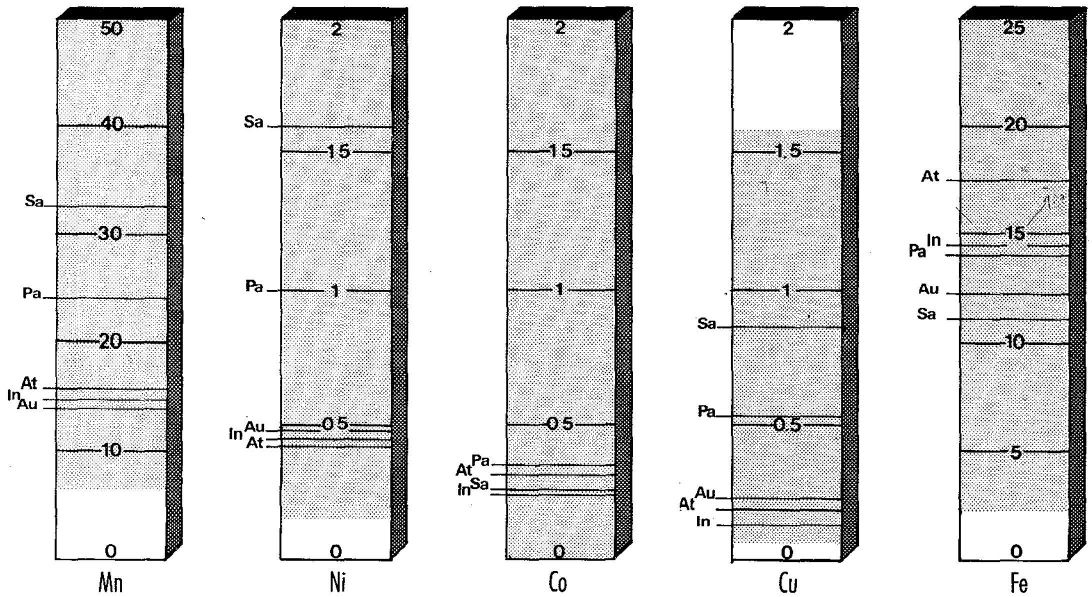
GEOGRAPHICAL LOCALIZATION OF NODULES DEPOSITS

Fig.1



CHEMICAL ANALYSIS OF DEAP-SEE NODULES (DRY PRODUCTS) WEIGHT PERCENT

Fig.2

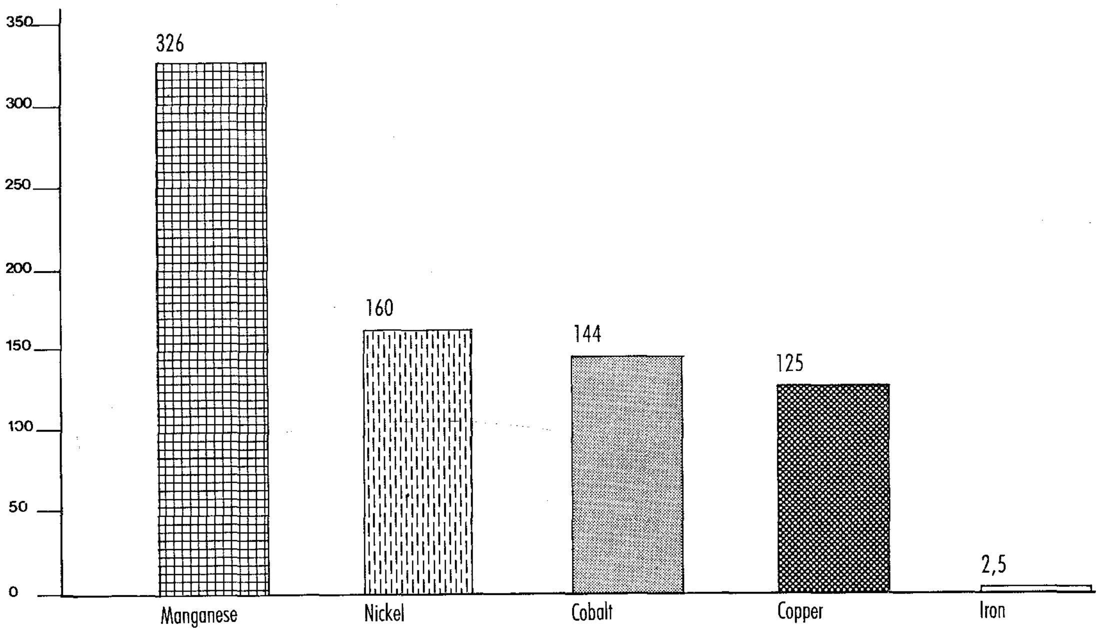


At = Average - Atlantic ocean
Au = Average - Austral ocean
In = Average - Indien ocean
Pa = Average - Pacific ocean
Sa = Sample used in this study

Extrema of composition observed

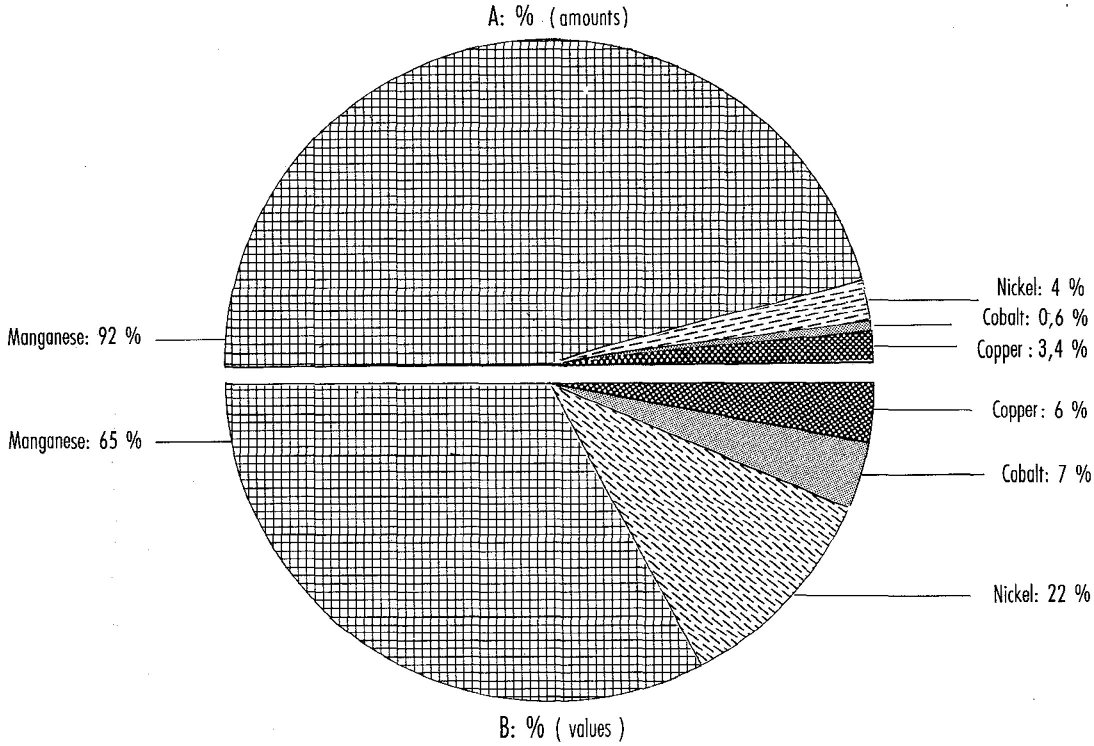
CLARKE OF COMPOSITION FOT THE MAIN METALS (this work sample - North Pacific CNEXO)

Fig.3



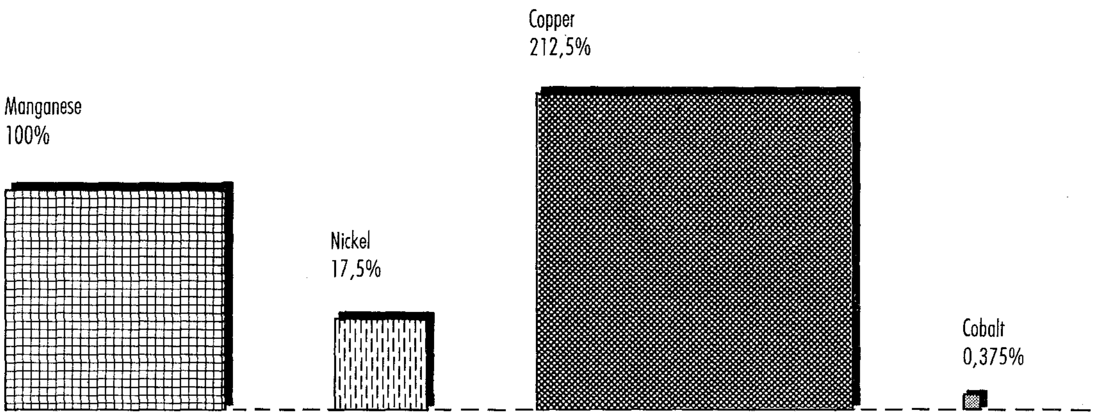
VALUABLE METALS AMOUNTS (A) AND VALUES (B) IN PERCENT OF THE TOTAL
(Analyses average for Pacific ocean nodules)

Fig.4



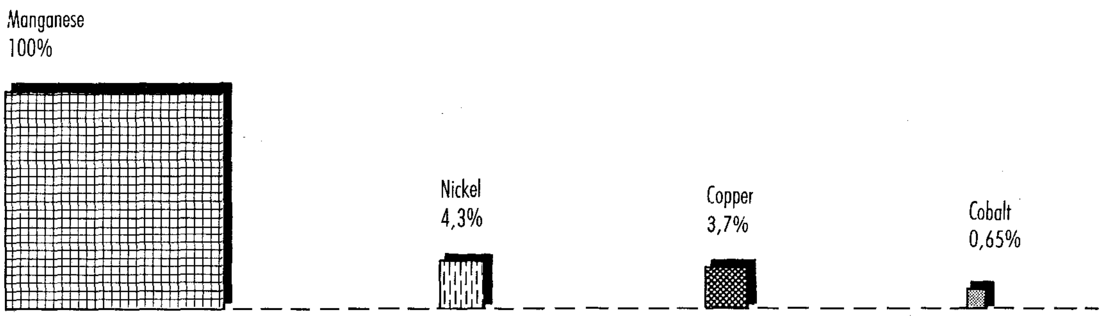
ANNUAL WORLD CONSUMPTION - MANGANESE = 100

Fig.5



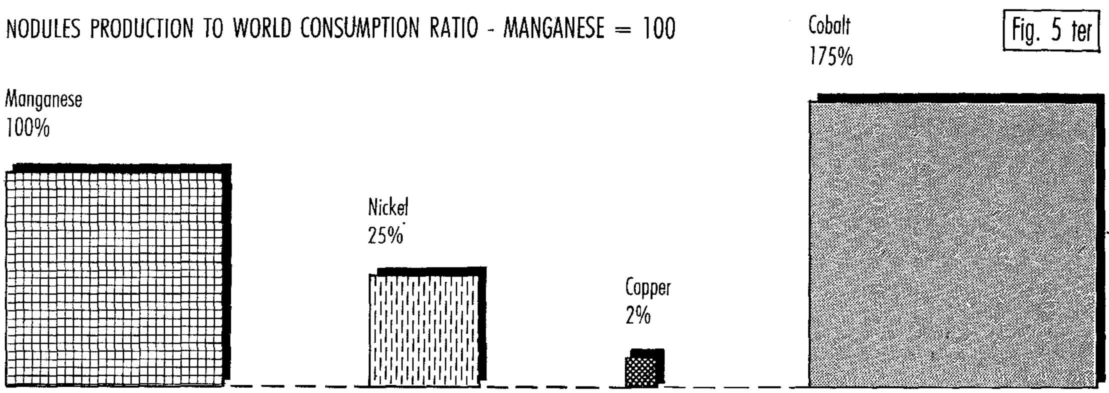
POSSIBLE PRODUCTION FROM NODULES - MANGANESE = 100

Fig.5 bis



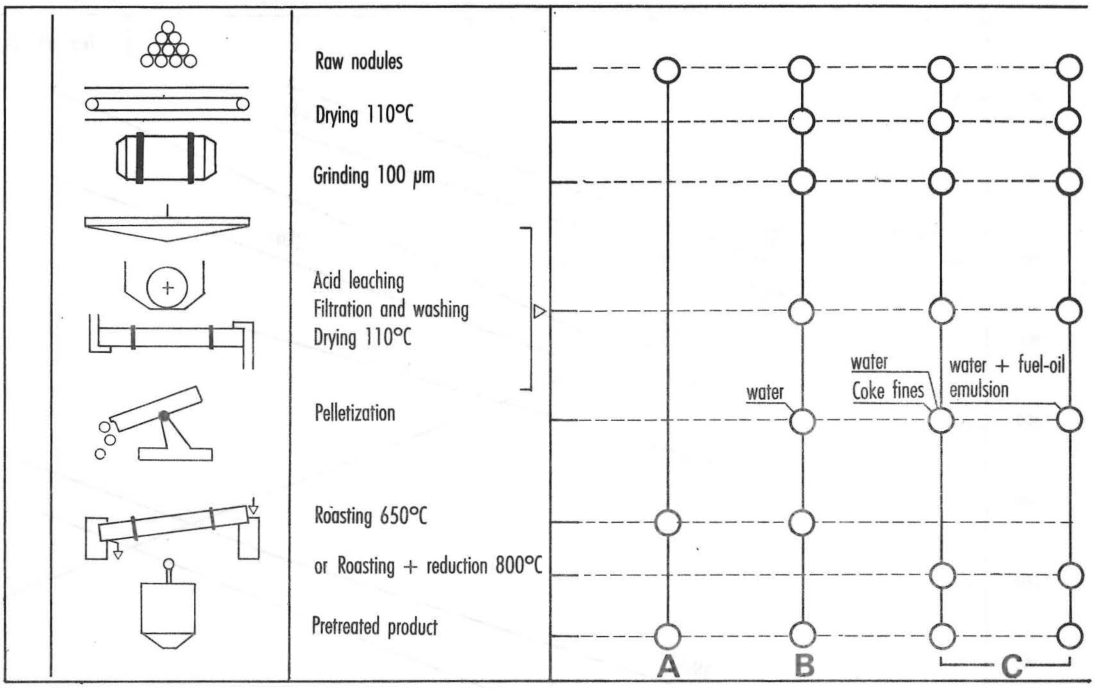
NODULES PRODUCTION TO WORLD CONSUMPTION RATIO - MANGANESE = 100

Fig. 5 ter



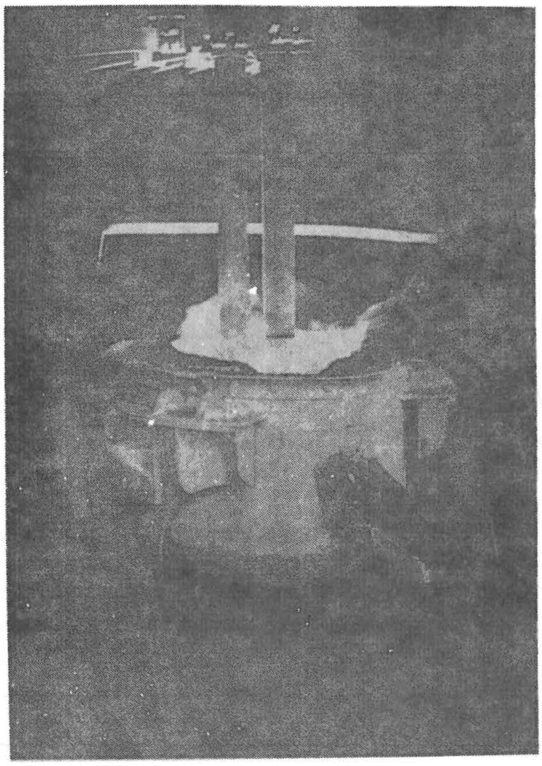
PRIOR PROCESSING OF NODULES

Fig.6



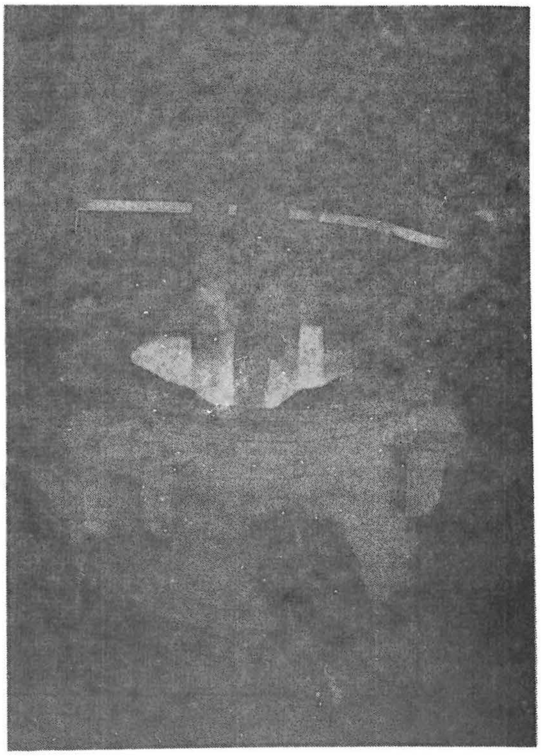
104 KVA TEST FURNACE - LOADING THE FURNACE

Fig.7



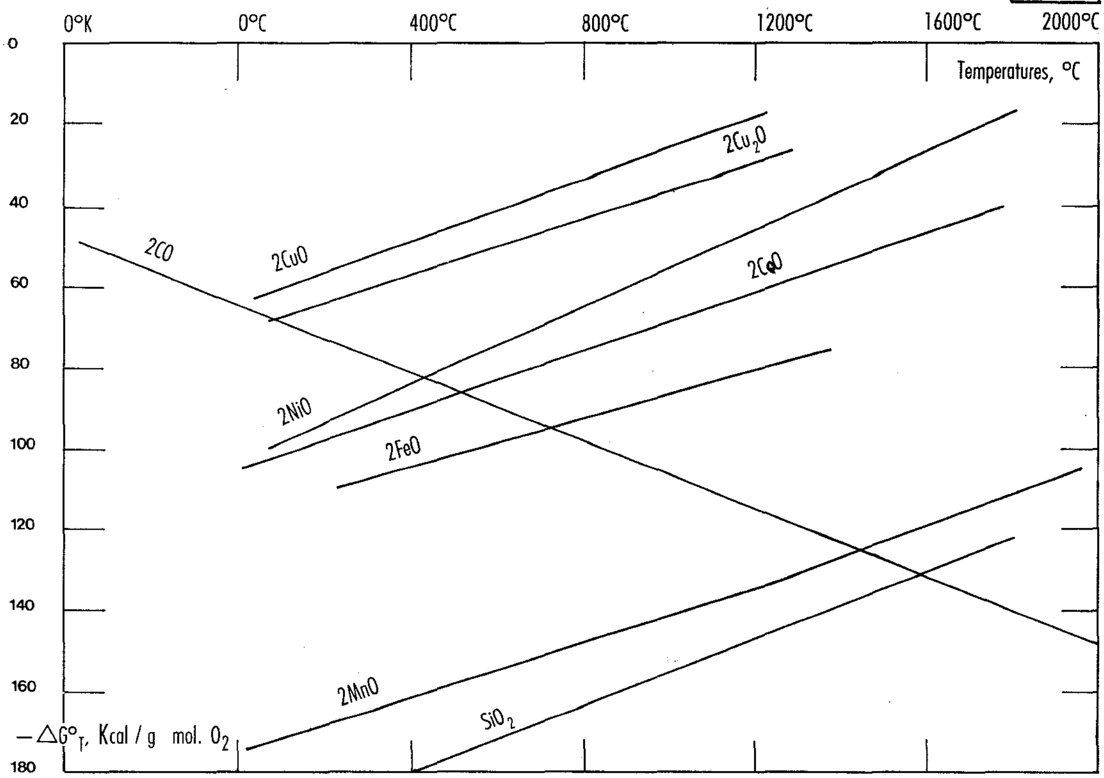
104 KVA FURNACE - SMELTING

Fig.8



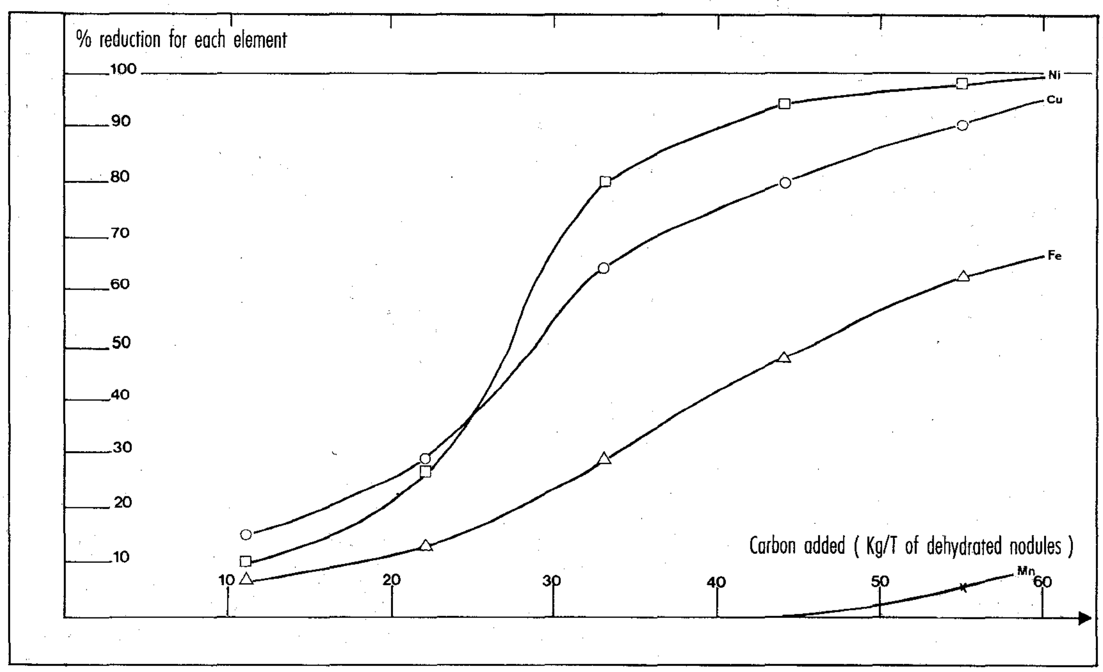
STANDARD FREE ENERGIES OF FORMATION OF SOME METAL OXIDES

Fig. 9



RESULTS OF REDUCTION TESTS

Fig. 10



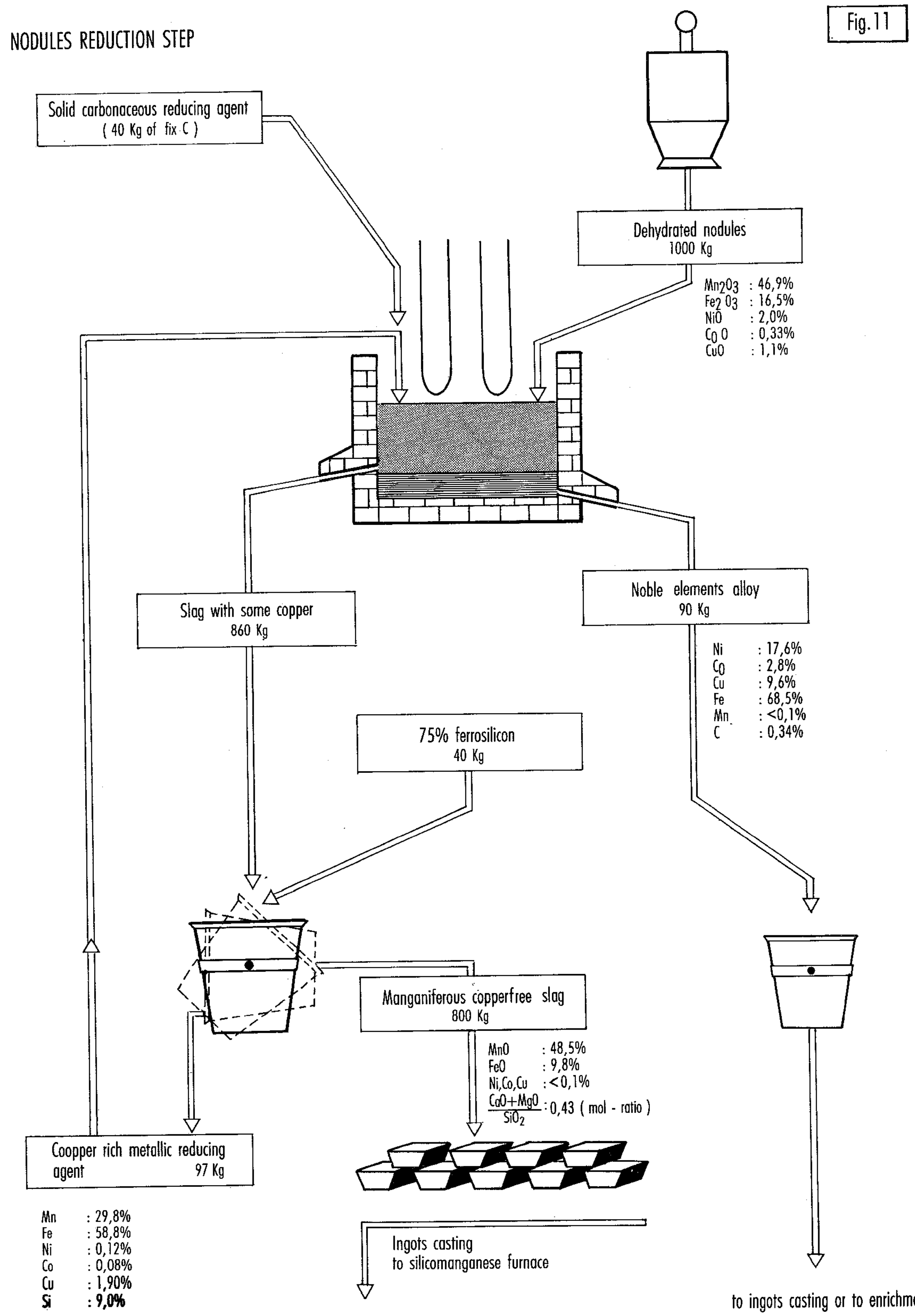
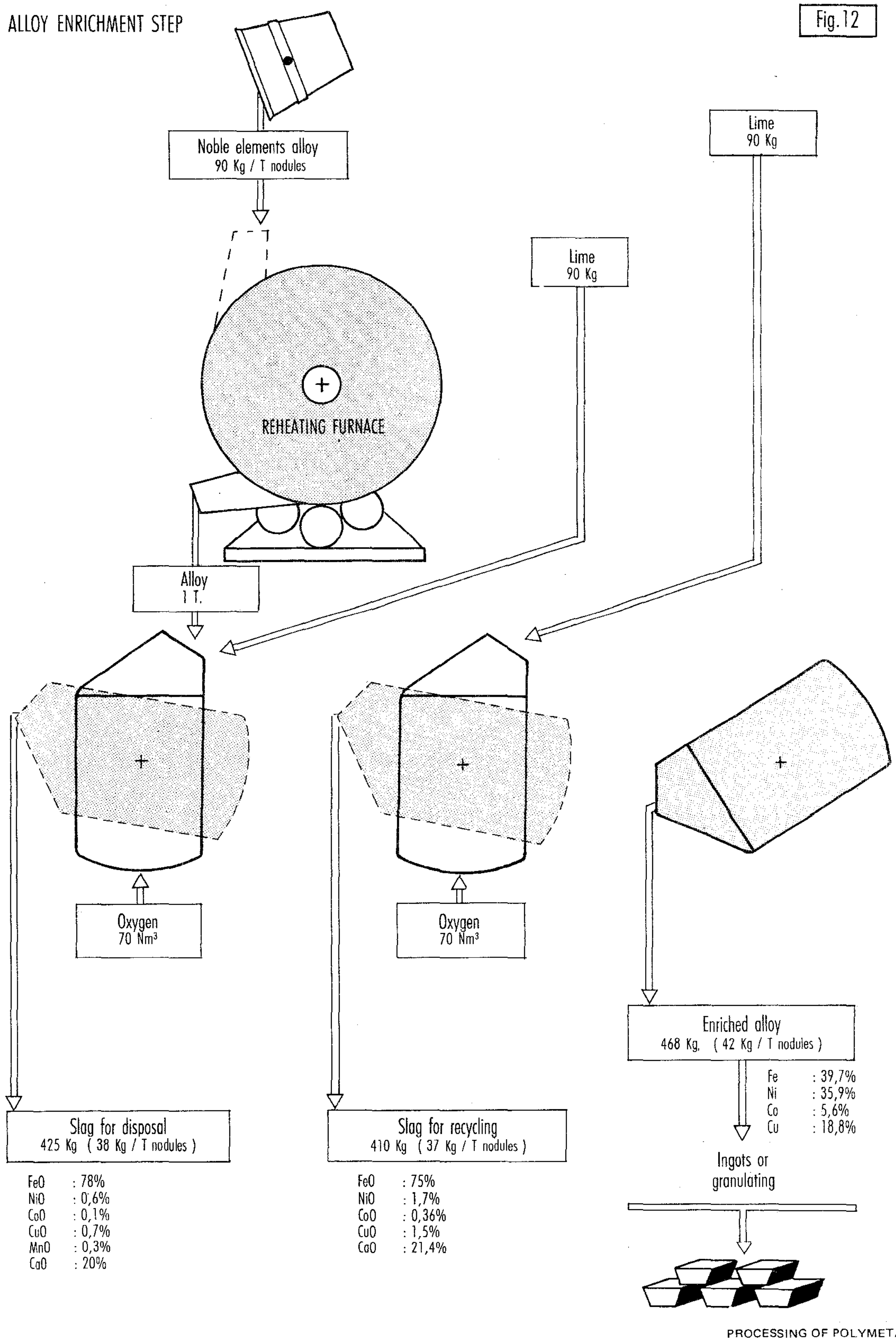


Fig.11
NODULES REDUCTION STEP
Solid carbonaceous reducing agent
(40 Kg of fix C)
Dehydrated nodules
1000 Kg
Mn_2O_3 : 46,9%
Fe_2O_3 : 16,5%
NiO : 2,0%
Co O : 0,33%
CuO : 1,1%
Slag with some copper
860 Kg
Noble elements alloy
90 Kg
Ni : 17,6%
Co : 2,8%
Cu : 9,6%
Fe : 68,5%
Mn : <0,1%
C : 0,34%
75% ferrosilicon
40 Kg
Manganiferous copperfree slag
800 Kg
MnO : 48,5%
FeO : 9,8%
Ni,Co,Cu : <0,1%
$\frac{CaO+MgO}{SiO_2}$: 0,43 (mol - ratio)
Coopper rich metallic reducing
agent 97 Kg
Mn : 29,8%
Fe : 58,8%
Ni : 0,12%
Co : 0,08%
Cu : 1,90%
Si : 9,0%
Ingots casting
to silicomanganese furnace
to ingots casting or to enrichment

ALLOY ENRICHMENT STEP

Fig. 12



SCHEMATIC FLOW DIAGRAM OF THE PROPOSED PROCESSING OF OCEAN NODULES

Fig. 13